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(71) Applicant:
Kolon Industries, Inc.
Kwacheon-city, Kyunggi-do 427-040 (KR)

(72) Inventors:
- **Shin, He Kuk**
  Seoungnam-city, Kyunggi-do (KR)
- **Hu, Chul**
  Yongin-city, Kyunggi-do (KR)

(74) Representative:
TER MEER STEINMEISTER & PARTNER GbR
Mauerkircherstrasse 45
81679 München (DE)

(54) A polysulfone based hollow fiber membrane, and a process for preparing the same

(57) The present invention relates to the production of a polysulfone based hollow fiber membrane, having a high water permeability coefficient and excellent permeability with no deterioration of separation capability, characterized by using an internal coagulating liquid and/or an external coagulating liquid containing diethylene glycol (DEG) and/or salt which can form a hydrate in the process of producing the polysulfone based hollow fiber membrane by following steps:

(a)Extrude a spinning dope comprising polysulfones resin, organic solvent and polyvinyl pyrrolidone (PVP) into air through a biannular spinning nozzle to obtain an extrudate in the form of a hollow fiber,

(b)Simultaneously inject an internal coagulating liquid into the biannular spinning nozzle at inside bore thereof, and

(c)Subsequently introduce said extrudate to an external coagulating liquid.

EP 0 927 572 A2

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a polysulfone based hollow fiber membrane and a process for preparing the same.

[0002] A large number of researches on the material of separation membrane which has selective permeability had been made, and celluloses, polyamides, polyacryls and polyvinyls have been developed for the membrane material and practically are in use. These material, however, have drawbacks such as bio-compatibility, chemical resistance, and heat resistance. In order to prevent these drawbacks, studies on adopting resins used for engineering plastics as separation membrane have been made, and engineering plastic resin like polysulfone based is in use as a material of separation membrane. Since the polysulfone based resin has excellent properties such as bio-compatibility, chemical resistance, heat resistance, flame resistance, and mechanical characteristics, it is widely used as a membrane materials for hemodialysis, micro filtration, ultra filtration, reverse osmosis, and gas separation.

[0003] Generally speaking, polysulfones hollow fiber membrane is produced by spining the Spinning Dope composed of polysulfones resin, organic solvent and additives such as water soluble polymer, and internal coagulating liquid into air through a biannular spinning nozzle to obtain an extrudate in the form of a hollow fiber, and then coagulate the said extrudate by external coagulating liquid.

[0004] In the process of producing the said Spinning Dope, m-cresol, N-methyl-2-pyrrolidone, dimethyl sulfoxide, dimethyl acetamide, dimethyl formamide and/or the mixture thereof are used for solvent.

[0005] Water soluble polymer is selected from polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone and/or the mixture.

[0006] Though water is usually used for both internal and external coagulating liquid, water solution comprising the said additives could be used for both internal and external coagulating liquid.

2. Description of the Prior Art

[0007] In respect to membrane, in general, the most important two properties are the capability of eliminating more than certain molecular weight of separation material(hereinafter called "separation capability") and permeability, but these two properties are not mutually compatible: if separation capability goes up, then permeability goes down relatively, and if permeability needs to be increased, then separation capability cannot but be lowered. Therefore, an important task of developing membrane is to produce a membrane which has certain separation capability and higher permeability at the same time.

[0008] First of all, in order to improve the permeability of a membrane, many large pores should be formed in membrane. In addition, in order to elevate the separation capability of a membrnae while it maintains certain permeability, the size of pores formed in membrane must be similar.

[0009] Up to date, several methods, adding water soluble polymer, solvent and/or alcohol compound in internal coagulating liquid and/or external coagulating liquid, have been in use to form pores in membrane. These methods, however, can not support to form similar size pores so as to meet the required certain level of separation capacity and permeability in hemodialysis membrane.

[0010] In the mean time, if the said water soluble polymer added in Spinnig Dope, remains quite a lot in hollow fiber membrane after the spinning process, the permeability, without deterioration in separation capability, shall be improved because of the elevated hydrophilicity of hollow fiber membrane. In fact, after the spinning process, most of water soluble polymer leaks to outside of hollow fiber membrane during coagulating and washing processes, and remains a little in the inside of hollow fiber membrane because of its' high solubility to water.

[0011] U.S. Patent No. 5,340,480 discloses that a water solution containing polyvinyl pyrrolidone shall be applied as internal coagulation liquid in order to leave polyvinyl pyrrolidone(hereinafter called "PVP"), the water soluble polymer, in the surface of hollow fiber membrane for improvement of permeability, but the efficiency is insignificant.

[0012] Japanese Patent Laid-Open No. 58-104940 discloses that use a cross linkage agent for fixing water soluble polymer to the surface of polysulfone hollow fiber membrane, but the process and operation is very complicating.

[0013] Japanese Patent Laid-Open Nos. 63-97205 and 63-97634 disclose that use heat treatment or radiant rays treatment for fixing water soluble polymer to the surface of polysulfone hollow fiber membrane, but the process is complicating and it requires expensive equipments.

[0014] Therefore, in order to improve the separation capability and permeability of the membrane at the same time, following techniques have been required to be developed:

1. A technique to form similar size of pores in membrane, and

2. A technique simply and effectively to leave water soluble polymer which was added in Spinning Dope, in hollow fiber membrane.

[0015] The present invention relates to produce a polysulfone based hollow fiber membrane comprising excellent separation capability, permeability and high water permeable coefficient by forming similar-sized many pores in a polysulfone based hollow fiber membrane and by leaving a lot of PVP, the water soluble polymer, in inside of membrane.

SUMMARY OF THE INVENTION

[0016] The present invention relates to a polysulfone based hollow fiber membrane mainly in use for hemodialysis, and a process for preparing the same.

[0017] More Particularly, the present invention relates to a process of producing a polysulfone based hollow fiber membrane characterized by using an internal coagulating liquid and/or an external coagulating liquid containing diethylene glycol(hereinafter called "DEG") and/or salt which can form a hydrate in the process of producing the polysulfone based hollow fiber membrane by following steps:

(a)Extrude a spinning dope comprising polysulfone based resin, organic solvent and PVP into air through a biannular spinning nozzle to obtain an extrudate in the form of a hollow fiber,
(b)Simultaneously inject an internal coagulating liquid into the biannular spinning nozzle at inside bore thereof, and
(c)Subsequently introduce said extrudate to an external coagulating liquid.

[0018] The present invention also relates to a polysulfone based hollow fiber membrane characterized that water permeable coefficient is at least 0.15 mℓ/minute/kgf/cm^2, cytochrome-C rejection rate is at most 30% , and myoglobin rejection rate is at least 80%.

[0019] Also the present invention relates to a polysulfone based hollow fiber membrane characterized that water permeable coefficient is at least 0.01 mℓ/minute/kgf/cm^2, cytochrome-C rejection rate is at least 80% , and vitamin B_{12} rejection rate is at most 50% .

[0020] The properties of polysulfone based hollow fiber membrane of the present invention are dependent on the containing quantity of DEG and salt which can form a hydrate in internal and/or external coagulating liquid.

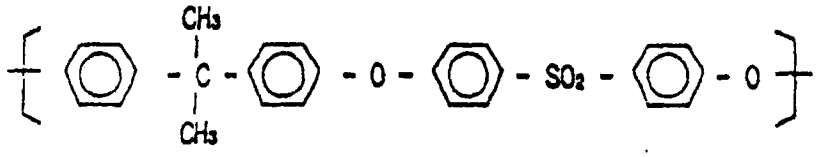
BRIEF DESCRIPTION OF THE DRAWING

[0021] Figure 1 is a rough drawing, expressing the mechanism of forming pore in hollow fiber membrane when $CaCl_2$ solution is applied for internal coagulating liquid and/or external coagulating liquid of the present invention.

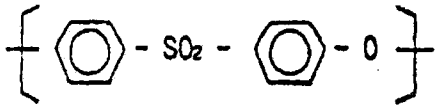
1 : Surface of membrane 2 : Hydrate of $CaCl_2$

DETAILED DESCRIPTION OF THE INVENTION

[0022] More concretely, the present invention is explained as follows. First of all, prepare spinning dope by dissloving polysulfone based resin in organic solvent and add PVP in the said organic solvent. In the process of preparing spinning dope, other additives could be added thereto. The polysulfone based resin in the present invention has a recurring unit represented by following formula. (I) or (II).



(I)



(II)

[0023] As for organic solvent, m-cresol, N-methyl-2-pyrrolidone, dimethyl sulfoxide, dimethyl acetamide, dimethyl formamide and/or the mixture thereof are applied.

[0024] Inorganic salt, alcohol compound, polyethylene glycol, and polyvinyl alcohol, could be used for additives selectively.

[0025] It is desirable that the said spinning dope is composed of 10~50 weight% of polysulfone based resin, 20~89 weight% of organic solvent, and 1~30 weight% of additives comprising PVP. But, the present invention does not specifically restrict the component ratio of spinning dope.

[0026] The next step is to prepare polysulfone based hollow fiber membrane by spinning the said spinning dope and internal coagulating liquid through biannular spinning nozzle to obtain extrudate, and coagulating the extrudate in external coagulating liquid, and washing, and winding. The biannular spinning nozzle has outside and inside diameter of 0.35mm and 0.15mm.

[0027] During the spinning process, extrude the polymer at the speed of 2.5g/minute, and maintain air gap at the level of 10cm or so. Internal coagulating liquid and/or external coagulating liquid applied in the above said process - in other word, at least one out of internal coagulating liquid and external coagulating liquid - has to use a solution comprising DEG, or salt which can form hydrate, or DEG and salt which can form hydrate at the same time. More preferably, at least one out of the said internal coagulating liquid and external coagulating liquid shall be water solution containing DEG, water solution containing salt which can form hydrate, or the water solution compound thereof. The said salt which can form hydrate is $CaCl_2$, $ZnCl_2$, $MgSO_4$, Na_2SO_4, and the most desirable one is $CaCl_2$.

[0028] During passing through process of hollow fiber membrane before coagulating of spinning dope, $CaCl_2$, $MgSO_4$, Na_2SO_4 and the like existing in the said internal coagulating liquid and/or external coagulating liquid exist in hydrated precipitation status because of hydrophobicity thereof(e.g. the hydrophobicity of membrane itself) and accelerate to form pores in the aforesaid membrane.

[0029] The pore in this process functions as a kind of pore core, it grows to certain size until the membrane coagulates completely. Consequently, the number of pore shall be increased, and the size also shall be similar. In this process, if coagulation deferring material of membrane(e.g. : Dimethylformamide) are added with $CaCl_2$, it is possible to enlarge the pore as desired size since the said pore getting bigger so much that the coagulation defers. However, the uniformity of pores shall be somewhat deteriorated. Therefore, it is possible to selectively add membrane coagulation deferring material such as dimethylformamide in internal coagulating liquid and/or external coagulating liquid depends on separation material.

[0030] In the mean time, if a water solution containing salt which cannot form hydrate like NaCl, is applied to internal coagulating liquid and/or external coagulating liquid, salt in coagulating liquid cannot pass through membrane because of a repulsion force originated in hydrophobicity of spinning dope.

[0031] However, a salt which can form hydrate like the present invention, it is possible to remove the said repulsion force, somewhat static electricity like, by the hydration of salt. As a result, it is possible to pass through the membrane.

[0032] Meanwhile, in the case internal coagulating liquid and/or external coagulating liquid, wherein DEG was not contained, are applied, most of PVP shall be leaked to outside of hollow fiber membrane during coagulating and washing processes after spinning because of its' high solubility to water.

[0033] That is to say, a little amount of PVP, which has not yet migrated to outside of polymer matrix during the said polysulfone based polymer rapidly coagulated in the process of spinning and coagulation, shall be remained inside of hollow fiber membrane.

[0034] Especially, as the surface of said membrane directly contacts with external coagulating liquid and be coagu-

lated rapidly, relatively much of PVP shall remain in the surface than the inside of membrane.

[0035] In the present invention, DEG contained in the internal coagulating liquid and/or external coagulating liquid deteriorates the solubility of PVP to coagulating liquid and water, and elevates the affinity with polysulfone based resin at the same time, it enables to increase the remaining quantity of PVP in the polysulfone based hollow fiber membrane.

[0036] A complex is made by hydrogen bond between functional group of pyrrolidone and -OH functional group of DEG.

[0037] Once the complex of PVP and DEG is formed as aforesaid, the solubility of PVP to coagulating liquid and water shall be downed, and then a large quantity of PVP shall be remained in the inside of polysulfone based hollow fiber membrane.

[0038] In case, the said complex is not formed, hydrophilic part of PVP remained in polymer matrix shall be aggregated in the inside of matrix, and hydrophobic part of PVP remained in polymer matrix shall be aggregated in the outside thereof by hydrophobicity itself of polysulfone based resin.

[0039] As result, the separation process shall be difficult.

[0040] Like the present invention, however, if the internal coagulating liquid and/or external coagulating liquid contain DEG, the above said problem shall be solved because of the complex made by PVP and DEG. In the present invention, it is possible to produce various polysulfone based hollow fibers having various properties by controlling the DEG content or salt content which can form hydrate added in internal coagulating liquid and/or external coagulating liquid, and ultimately by controlling the pore size and the content of hydrophilic material remained in the inside of membrane.

[0041] More concretely, if the DEG content of internal coagulating liquid and/or external coagulating liquid is less than 90 weight%, or if salt content which can form hydrate is less than 40 weight%, a permeability, so called water permeable coefficient shall be downed to some extent, but separation capability shall be improved. In this case, the said produced polysulfone based hollow fiber membrane has following properties;

- at least 0.01 mℓ/minute/kgf/cm^2 of water permeable coefficient,
- at least 80% of Cytochrome-C rejection rate, and
- at most 50% of Vitamin B_{12} rejection rate.

[0042] In the mean time, if the DEG content of internal coagulating liquid and/or external coagulating liquid is at least 90 weight%, or if salt content which can form hydrate is at least 40 weight%, a permeability, so called water permeable coefficient shall be improved, but separation capability shall be downed to some extent. In this case, the said produced polysulfone based hollow fiber membrane has following properties;

- at least 0.15 mℓ/minute/kgf/cm^2 of water permeable coefficient,
- at most 30% of Cytochrome-C rejection rate, and
- at least 80% of Myoglobin rejection rate.

[0043] Because of a polysulfone based hollow fiber membrane produced in the way of present invention has many similar-sized pores, it has excellent permeability and separation capability at the same time.

[0044] The fact that pores formed in the membrane are similar, can be learned by big difference of respective rejection rates in measuring two kinds of separation material which has different molecular weight.

[0045] Because of a polysulfone based hollow fiber membrane produced in the way of present invention has higher hydrophilicity, it has relatively excellent permeability comparing to other membrane which has similar rejection rate(in other words, which has similar pore size). That is to say, the effectiveness of separation process shall be improved without deteriorating the separation capability due to its' elevated permeability.

[0046] As it is possible to reject material selectively in desired size from a solution, wherein several material has been mixed, Polysulfone based hollow fiber membrane of the present invention can be applied very effectively to the medical fields like artificial kidney.

[0047] Water permeable coefficient and separation material rejection rate of the present invention shall be measured in the following manner:

• Evaluation of water permeable coefficient

[0048] Prepare small glass tube like module by filling 20 ply of hollow fiber(length : 15cm). And then calculate the water permeability(mℓ /minute/kgf/cm^2) in maintaining pressure of membrane in-between at 1 kgf or so.

• Evaluationof separation material rejection rate

[0049] Measure the concentration of separation material in water solution as to before and after permeating hollow

fiber membrane, and then calculate the separation material rejection rate by following equatation.

$$\text{Separation Material Rejection Rate(\%)} = \frac{A - B}{A} \times 100$$

In the above equation, A is the concentration of separation material in water solution before permeating hollow fiber membrane, and B is the concentration of separation material in water solution after permeating hollow fiber membrane.

[0050] More concretely, the present invention shall be examined through following examples and comparative examples. The present invention, however, does not restrict only to following examples:

Example 1

[0051] After add 17 weight% of polysulfone resin(P-3500 : product of Amoco Co.), 10 weight% of polyvinyl pyrrolidone, and 9 weight% of polyethyleneglycol to 64weight% of dimethylformamide, then produce transparent spinning dope by mixing and dissolving.

[0052] Extrude the said spinnig dope through external nozzle out of biannular spinning nozzle having 0.35mm of outside diameter, and 0.15mm of inner nozzle diameter at the speed of 2.5g/minute, and simultaneously extrude $CaCl_2$/water solution(30wt%/70 wt%), the internal coagulating liquid through internal nozzle out of the said biannular spinning nozzle at the speed of 2.4g/minute. After pass through the said extruded hollow fiber into 10 cm air gap, prepare polysulfone hollow fiber by coagulating and washing, in water(external coagulating liquid), and winding at the speed of 50m/minute. Produce polysulfone hollow fiber membrane by introducing the aforesaid polysulfone hollow fiber in module. Result of measurement for separation capability and permeability of the produced polysulfone hollow fiber membrane is shown at Table 2.

Examples 2 ~ 6, and Comparative Examples1 ~ 4

[0053] Produce polysulfone hollow fiber membrane in same process and condition as Example 1, except the changes of composition to internal coagulating liquid and/or external coagulating liquid as shown at Table 1. Results of measurement for separation capabilities and permeabilities of the produced polysulfone hollow fiber membranes are shown at Table 2.

〈Table 1〉

	Production Composition	
	Internal Coagulating Liquid	**External Coagulating Liquid**
Example 1	$CaCl_2$ / water Solution (30 wt% / 70 wt%)	Water
Example 2	$CaCl_2$ / water Solution (30 wt% / 70 wt%)	$CaCl_2$ / water Solution (30 wt% / 70 wt%)
Example 3	DEG / water Solution (80 wt% / 20 wt%)	Water
Example 4	DEG / water Solution (80 wt% / 20 wt%)	DEG / water Solution (80 wt% / 20 wt%)
Example 5	DEG / water Solution (95 wt% / 5 wt%)	Water
Example 6	CaC_2/DEG/Water Solution (4wt% / 90wt% / 6wt%)	Water
Comparative Example 1	Methanol	Water
Comparative Example 2	polyethylene glycol / water Solution (70 wt% / 30 wt%)	Water
Comparative Example 3	Dimethylform amide / water Solution (60 wt% / 40 wt%)	Water
Comparative Example 4	Dimethylform amide / water Solution (70 wt% / 30 wt%)	Water

〈Table 2〉

Result of measurement for separation capability and permeability				
	Vitamin B12 Rejection Rate(%) [Molecular Weight: 1,300]	Cytochrome-C Rejection Rate(%) [Molecular Weight: 12,400]	Myoglobin Rejection Rate(%) [Molecular Weight: 18,800]	Water Permeable Coefficient [ml/min/kgf/cm^2]
Example 1	40	97	-	0.015
Example 2	35	98	-	0.016
Example 3	41	90	-	0.025
Example 4	30	85	-	0.025
Example 5	-	20	80	0.25
Example 6	-	15	85	0.21
Comparative Example 1	70	92	-	0.0082
Comparative Example 2	60	91	-	0.0093
Comparative Example 3	-	15	40	0.1
Comparative Example 4	-	5	10	0.2

[0054] Though all Cytochrome-C(molecular weight 12,400) rejection rates of polysulfone hollow fiber membrane produced in the ways of examples 1 ~ 4, and comparative examples 1 ~ 2 are over than 80%, but examples 1 ~ 4 have better permeabilities than those of comparative examples 1 ~ 2 due to higher water permeable coefficients.

[0055] In addition, though all Cytochrome-C(molecular weight 12,400) rejection rates of polysulfone hollow fiber membrane produced in the ways of examples 5 ~ 6, and comparative examples 3 ~ 4 are less than 30%, but examples 5 ~ 6 have better selectivity than comparative examples 3 ~ 4 due to higher water permeable coefficients, and higher difference of rejection rates between two material which have different molecular weights.

[0056] Polysulfone based hollow fiber membrane of the present invention not only has excellent permeability due to formed many similar size pores or more existence of hydrophilic material but also has excellent separation capability due to similar size pores with higher water permeable coefficient than other hollow fiber membrane which has similar size pores.

Claims

1. A process of producing a polysulfone based hollow fiber membrane characterized by using an internal coagulating liquid and/or an external coagulating liquid containing diethylene glycol(DEG) and/or salt which can form a hydrate in the process of producing the polysulfone based hollow fiber membrane by following steps:

   (a)Extrude a spinning dope comprising polysulfones resin, organic solvent and polyvinyl pyrrolidone(PVP) into air through a biannular spinning nozzle to obtain an extrudate in the form of a hollow fiber,
   (b)Simiultaneously inject an internal coagulating liquid into the biannular spinning nozzle at inside bore thereof, and
   (c)Subsequently introduce said extrudate to an external coagulating liquid.

2. A process of producing a polysulfone based hollow fiber membrane according to claim 1, wherein the said salt which can form a hydrate, is $CaCl_2$, $MgSO_4$, Na_2SO_4, and $ZnCl_2$.

3. A process of producing a polysulfone based hollow fiber membrane according to claim 1, wherein the said salt which can form a hydrate, is $CaCl_2$.

4. A process of producing a polysulfone based hollow fiber membrane according to claim 1, wherein the said internal coagulating liquid and/or external coagulating liquid is a water solution containing dietylene glycol(DEG).

5. A process of producing a polysulfone based hollow fiber membrane according to claim 1, wherein the said internal coagulating liquid and/or external coagulating liquid is a water solution containing salt which can form a hydrate.

6. A process of producing a polysulfone based hollow fiber membrane according to claim 1, wherein the said polysulfones resin is polysulfone resin or polyethersulfone resin.

7. A polysulfone based type hollow fiber membrane characterized by water permeable coefficient is at least 0.01 mℓ/minute/kgf/cm^2, cytochrome-C rejection rate is at least 80% , and vitamin B_{12} rejection rate is at most 50%.

8. A polysulfone based hollow fiber membrane characterized by the water permeable coefficient is at least 0.15 mℓ/minute/kgf/cm^2, cytochrome-C rejection rate is at most 30% and myoglobin rejection rate is at least 80%.

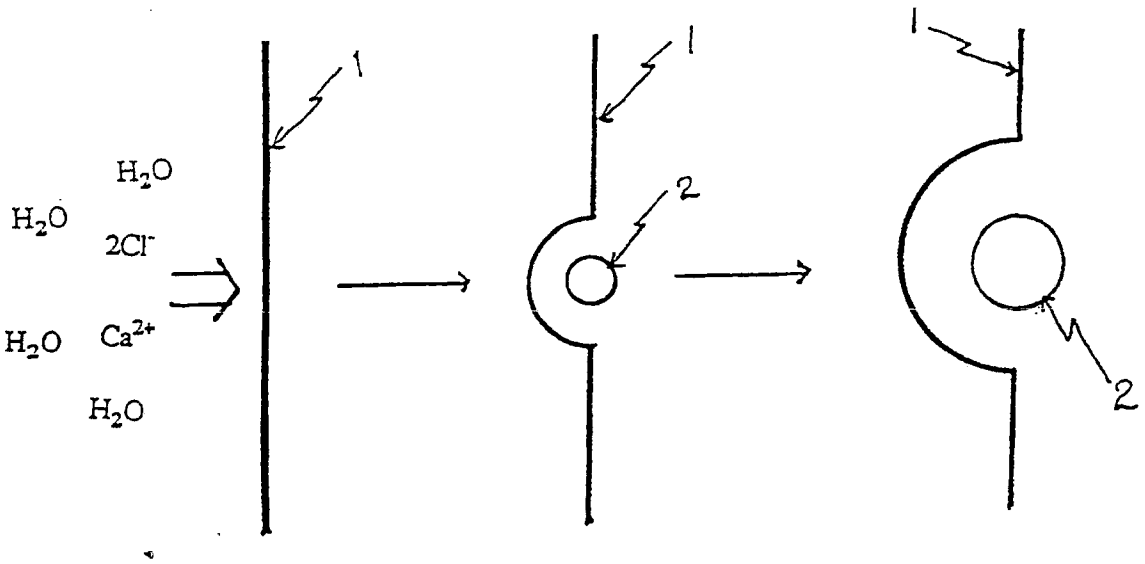


Fig. 1

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(71) Applicant:
Kolon Industries, Inc.
Kwacheon-city, Kyunggi-do 427-040 (KR)

(72) Inventors:
- **Shin, He Kuk**
  Seoungnam-city, Kyunggi-do (KR)
- **Hu, Chul**
  Yongin-city, Kyunggi-do (KR)

(74) Representative:
TER MEER STEINMEISTER & PARTNER GbR
Mauerkircherstrasse 45
81679 München (DE)

(54) A polysulfone based hollow fiber membrane, and a process for preparing the same

(57) The present invention relates to the production of a polysulfone based hollow fiber membrane, having a high water permeability coefficient and excellent permeability with no deterioration of separation capability, characterized by using an internal coagulating liquid and/or an external coagulating liquid containing diethylene glycol (DEG) and/or salt which can form a hydrate in the process of producing the polysulfone based hollow fiber membrane by following steps:

(a)Extrude a spinning dope comprising polysulfones resin, organic solvent and polyvinyl pyrrolidone (PVP) into air through a biannular spinning nozzle to obtain an extrudate in the form of a hollow fiber,

(b)Simultaneously inject an internal coagulating liquid into the biannular spinning nozzle at inside bore thereof, and

(c)Subsequently introduce said extrudate to an external coagulating liquid.

EP 0 927 572 A3

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EUROPEAN SEARCH REPORT

Application Number
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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B01D
D01D
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM P0459